A NOTE ON THE RELAXATION TIMES OF THE PROTON IN CANE SUGAR SOLUTION AND GLYCERINE WITH ADDED PARAMAGNETIC Cu^{++} IONS(*)

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ABSTRACT. The spin-lattice relaxation time of the proton has been determined from Bloombergen's formula, in which the numerical factor has been modified to take into account the interactions arising in the case of cane sugar solution and glycerine with added Cu^{++} ions. The spin-spin relaxation time could be estimated from measurements of n.m.r. signal strength. It has been shown that in both of these liquids, T_1 and T_2 are of the order of 10^{-4} sec.

Bloembergen, Purcell and Pound (1948) have propounded a theory of nuclear magnetic relaxation, which was successfully applied by them to pure liquids including, among others, water, glycerine, ethyl alcohol etc. These authors have also extended their theory to the case of dilute aqueous solutions of paramagnetic ions like Cu^{++}, Fe^{+++} etc., and have been successful in explaining the reduction in the spin-lattice relaxation time T_1 of protons in these media, which was first observed by Bloch, Hansen and Packard (1946). The magnetic moment of a paramagnetic ion is of the order of one Bohr magneton, which is about 1840 times bigger than the nuclear magneton. Therefore, on addition of these ions to a liquid like H_2O, the intermolecular magnetic interaction between a liquid molecule and a neighbouring ion largely predominates over the intramolecular interaction between the two protons in the same molecule.

In a previous work Mukherjee, (1964) we have reported measurements of nuclear magnetic resonance signals in aqueous cane sugar solution and glycerine, both containing very small quantities of dissolved paramegnetic Cu^{++} ions. Our sample of glycerine ($C_3H_8O_3$) was 97.5% pure by weight (density at room temperature = 1.251g. cm^{-3}) and contained about 2.2×10^{18} Cu^{++} ions dissolved per cm^3 of the medium. From tables (4), the value of its viscosity was found to be $\eta = 6.6$ Poise at 23°C, so that $\eta/T = 2.2\times10^{-2}$P/°K, where T denotes the temperature in degrees Kelvin. The n.m.r. frequency was 15.5 Mcs./sec. If our glycerine sample did not contain Cu^{++} ions, its spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 should very closely follow the same dependence on η/T respectively as the T_1 and T_2 of the 98% pure glycerine (5) investigated by Bloembergen *et al*(*). Using Bloembergen's data we find,

(*) the attention of the reader is drawn to Fig. 13 on page 705 of the article by Bloembergen et al (1948).

that in our case, T_1 and T_2 are both independent of the n.m.r. frequency and $T_1 \approx T_2 \approx 2 \times 10^{-2}$ sec.

However, due to the presence of Cu^{++} ions, the relaxation times will be reduced. To account for the reduction in the value of T_1, we propose the following formula :

$$1/T_1 = 9.6\pi^2\gamma_p^2\eta N_i\mu_i^2/kT \quad \ldots \quad (1)$$

where γ_p is the gyromagnetic ratio of the proton, η is the viscosity of the medium, N_i is the number of ions per cm^3 of the medium, μ_i is the magnetic moment of the paramagnetic ion, k is the Boltzmann's constant and T, the absolute temperature. This equation differs by a numerical factor only from a similar equation given by Bloembergen *et al* (1948) for the T_1 of protons in H_2O. In modifying his equation, we have assumed that 8 protons are available for interaction with one Cu^{++} ion, i.e., one ion interacts magnetically with one molecule of glycerine and, as usual, the diffusion constant D is the same for the glycerine molecules and the divalent Cu^{++} ions. Assuming $\mu_i = 1.9$ Bohr magnetons (6) and putting numerical values in equation (1), we get $T_1 = 1.3 \times 10^{-4}$ sec. The order of magnitude of T_1 thus calculated, seems to be reasonable and our calculation shows that T_1 has been reduced by a factor of the order of 100 due to the influence of Cu^{++} ions. It must be mentioned, however, that the modification as represented by equation (1) is based purely on phenomenological considerations. However, the use of this equation appears to be justified by the fact that it apparently gives results of the correct order of magnitude.

According to Bloembergen's theory of the relaxation times of the proton in a liquid medium under conditions of resonance absorption,

$$T_2 \approx T_1 \quad \ldots \quad (2)$$

if

$$(2\pi\nu_0\tau_c)^2 << 1 \quad \ldots \quad (3)$$

Here ν_0 is the n.m.r. frequency and τ_c, the so-called "correlation time" given by

$$\tau_c = 4\pi\eta\alpha^3/3kT \quad \ldots \quad (4)$$

In this equation, α is the radius of the molecule containing the protons and all other symbols have been explained previously. Solomon (1955) has deduced on theoretical grounds that in a similar system of two nuclear spins, containing paramagnetic ions in solution, T_2 and T_1 are approximately equal if the same condition (3) holds good. It has also been shown experimentally by various workers including Bloembergen *et al*, (1948) Gabillard (1952) and Chiarotti and Giulotto (1953), that such an ionic concentration as used by us, T_2 is approximately equal to T_1 in aqueous paramagnetic solutions. Some of these authors used Cu^{++} ions, but many preferred Fe^{+++} ions.

In a medium like glycerine, when free from paramagnetic ions, the spinspin relaxation time T_2 which is a measure of the reciprocal of the resonance

line-width, arises from (i) a contribution due to the local magnetic fields of the nuclei (ii) a second contribution due to the mutual energy exchange in a spin-spin interaction process between the eight protons in the molecule and (iii) a third contribution given by $2T_1$, which measures the life-time of a nucleus in a particular excited state. (iv) There may be a fourth contribution to T_2 arising from a linebroadening due to the inhomogeneity of the magnetic field over the bulk of the sample. However, due to the presence of Cu^{++} ions in glycerine at the level indicated and the consequent reduction in the value of T_1, it is reasonable to assume that the contributions (i) and (ii), which are roughly equal, are of the same order of magnitude as the contribution (iii).

In our previous work (Mukherjee 1964), the n.m.r. coil was small (about 1.9 cm long compared to the pole-face diameter of 20.2 cm) and placed at the centre of the field. An accuracy of a few parts in 10^4 was obtained there in the determination of the ratio of the Larmor frequencies of the 1_H and 19_F nuclei. An estimation of the variation of the magnetic field in the medial plane of the air-gap, as one moves away from the centre along a radius, had been made by Guptill *et al* (1950). All these data lead us to believe that the magnetic field is homogeneous to within $\pm 0.03\%$. This value of field inhomogeneity allows us to calculate a line broadening, whose contribution to T_2 is 1.2×10^{-4} sec. (contribution iv). This figure is almost equal to the value of T_1 calculated from relation (1). Thus, although the glycerine molecule is a system of 8 "effective" nuclear spins, complicated by the presence of Cu^{++} ions, it is justified to assume that the total absorption line width is given by the reciprocal of T_1, at least, as far as the order of magnitude is concerned. Therefore, we can put, $T_2 \approx T_1 \approx 1.3\times10^{-4}$ sec. and $T_2/T_1 \approx 1$.

The cane sugar sample used by us had 53.5% by weight of $C_{12}H_{22}O_{11}$ dissolved in water and contained about 2.23×10^{18} Cu^{++} ions per cm^3 of the solution. This number is almost the same as that in the case of glycerine. Measurements were made of the density and viscosity of this solution at room temperature and gave following values : $\rho = 1.254$g. cm^{-3} and $\eta_s = 20.3$ cP (at 23°C). Cane sugar molecules containing 22 protons are bigger than glycerine molecules. The system contains, in addition, the cupric ions and a relatively large amount of water. Rougly speaking, 1 cm^3 of cane sugar solution contains, beside the cupric ions, about 1.95×10^{22} molecules of H_2O and 1.18×10^{21} molecules of $C_{12}H_{22}O_{11}$. Therefore, on the average, one Cu^{++} ion can be considered to be in the neighbourhood of 1 molecule of $C_{12}H_{22}O_{11}$ and 16 to 17 molecules of H_2O. Hence, effectively the magnetic interaction takes place between one Cu^{++} ion and about 55 protons. Keeping this simplified picture in mind and assuming, as before, the thermal diffusion coefficients of the ion and the two different types of molecules are approximately the same, we can modify the numerical factor in Bloembergen's formula for T_1. The modified formula now reads :

$$1/T_1 = 66\pi^2\gamma_p^2\eta_s N_i\mu_i^2/kT \qquad (5)$$

In this modification of Bloembergen's formula, the same phenomenological arguments have been followed as in the previous case.

In the cane sugar system $\eta_s/T = 6.9\times10^{-4}P/°K$. Substituting numerical values in equation (5), we get $T_1 = 6.2\times10^{-4}$ sec. The radius α of the cane sugar molecule can be estimated from its molar volume, namely, $\alpha = 4.4\times10^{-8}$ cm. Substituting in relation (4), we get $\tau_c \approx 1.8\times10^{-9}$ sec.(†). With the value of $\nu_0 = 15.4\times10^6$ c.p.s., the frequency used in this experiment, we get

$$(2\pi\nu_0\tau_c)^2 \approx 2.9\times10^{-2}, \text{ i.e. } << 1$$

Hence, from relation (2), we get, for protons in cane sugar solution, $T_2 \approx T_1$ ($\approx 6.2\times10^{-4}$ sec.).

The n.m.r. signal to noise voltage ratio is given by the following expression (1.11) :

$$\frac{V_s}{V_n} = \frac{y\zeta N\gamma_p I(1+1)\hbar^2}{48kT} \times \left(\frac{V_c Q\nu_0^3}{kTBF}\right)^{\frac{1}{2}} \times \left(\frac{T_2}{T_1}\right)^{\frac{1}{2}} \quad \ldots \quad (6)$$

In this expression γ_p, k, T, ν_0, T_1 and T_2 have the previous significance, y depends on the law of signal detection and ≈ 1, ζ is the "filling factor" of our coil (≈ 0.503) N is the number of protons per cm^3 ($N = 6.58\times10^{22}$ for glycerine; $N = 6.5\times10^{22}$ for cane sugar solution); I is the proton spin ($= 1/2$); $\hbar$ is the Planck's constant. V_c is approximately equal to the volume of the sample coil (≈ 3.32 cm^3), Q is the quality factor of this coil (≈ 253 at 15 Mcs./sec.) ν_0 is 15.5 Mcs./sec. for glycerine and 15.4 Mcs./sec. for cane sugar solution. B is the band width of the indicating instrument, namely, the level recorder used in our experiment (3) and $B \approx 6.1$ c.p.s. (measured value). F is the effective noise figure of the amplifier system. It has not been possible to measure F and we have eliminated this factor by making comparative measurements under almost identical adjustments of all parts of the apparatus.

As mentioned in the previous report (3), we get, at 23°C, 20 lg (V_s/V_n) equal to 14.0 db. for glycerine and 12.2db. for cane sugar solution, both containing almost equal amount of Cu^{++} ions, as aforesaid. On substitution of numerical values in relation (6) we now get, (T_2/T_1) in glycerine $= 1.43\times(T_2/T_1)$ in cane sugar solution. However, it has been shown above that (T_2/T_1) in cane sugar solution is ≈ 1 and T_1 in glycerine $\approx 1.3\times10^{-4}$ sec. It follows that T_2 in glucerine is 1.9×10^{-4} sec. This value of T_2 in glycerine has the same order of magnitude as that assigned to it in the same liquid, namely $T_2 = 1.3\times10^{-4}$ sec., elsewhere in this paper. This fact supports our assumption about the near equality of T_2 and T_1 in glycerine and cane sugar solution in the presence of paramagnetic ions.

(†) For water molecules in the same system, we get $\tau_c \approx 5.7\times10^{-11}$ sec.

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